Supporting Information for:

Response vs. Chain Length of Alkanethiol-Capped Au Nanoparticle Chemiresistive Chemical Vapor Sensors

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Appendix A.

The concentration of analyte sorbed into the sensing material at equilibrium can be calculated by using the K value of the analyte/material, given by:

$$K \equiv \frac{C_{\mathrm{A,film}}}{C_{\mathrm{V}}} \tag{1}$$

where $C_{\mathrm{A,film}}$ (mol L^{-1}) is the concentration of analyte in the film and $C_{\mathrm{A,V}}$ (mol L^{-1}) is the concentration of analyte in the vapor phase. $C_{\mathrm{A,flim}}$ is obtained with the value of K in conjunction with the use of $P/P°$ to calculate C_{V} through the ideal gas equation ($P/RT = C_{\mathrm{V}}$). Because it is assumed that sorption can only take place at the organic layer, the ligand concentration, C_{ligand}, in the film can obtained from the density of the condensed ligand (~ 0.84 g/ml). The sorbed analyte mole ratio is then:

$$X_n \approx \frac{C_{\mathrm{A,film}}}{C_{\mathrm{ligand}} + C_{\mathrm{A,film}}} \tag{2}$$

Figure S3 shows the value of X_{n} for Hex, Tol, EtOAc and BuOH. As $P/P°$ increased, higher values of X_{n} were obtained, as expected.

The dielectric constant of a mixture of two components depends on the volume fraction of both components, γ_1 and γ_2. For a given mixture of two substances having dielectric constants ε_1 and ε_2, respectively:[49]

$$\gamma_1 + \gamma_2 = 1 \tag{3}$$

For independent substances, having D_1 and D_2, the 2-component value of the electric displacement is given by $D = \gamma_1 D_1 + \gamma_2 D_2$. The electric field, E, throughout the mixture is given by $E = \gamma_1 E_1 + \gamma_2 E_2$. Hence, the resulting dielectric constant of the mixture is given by:

$$\varepsilon_{\mathrm{s}} = D/E \tag{4}$$

where for each component, $D_1 = \varepsilon_1 E_1$ and $D_2 = \varepsilon_2 E_2$.[49] Reynolds et al. demonstrated that an expression describing ε_{s} for a mixture of two components can be derived:

$$\varepsilon_{\mathrm{s}} = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2)\gamma_1 F_1 \tag{5}$$

where $F_1 = E_1/E$, which is assumed to approach unity. X_n can be used to estimate the value of γ_1 (i.e. vapor sorbted) and $X_{ligand} = 1 - X_n$.

Table S1. Partial pressure values as a function of temperature for *n*-hexane and ethanol.

Temperature (° C)	Hex (P/P° x 10^3)	EtOH (P/P° x 10^3)
4	2.7	3.8
11	1.9	2.4
18	1.4	1.5
25	1.0	1.0
32	0.74	0.67
39	0.56	0.46

Figure S1. Thermogravimmetric analysis of alkanethiol capped Au-NP films.

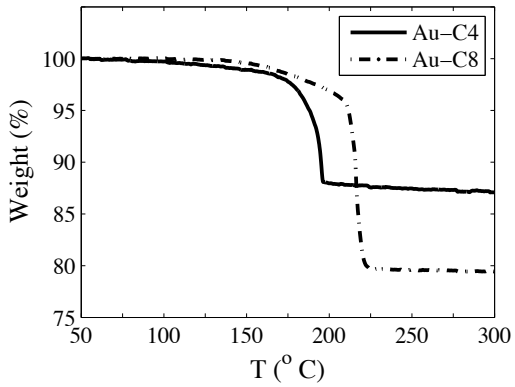


Figure S2. Baseline corrected single responses for a resistance change response (black) and the baseline-corrected response (red) for a Au-C8 sensor due to sorption of hexane ($P/P°$= 0.0010).

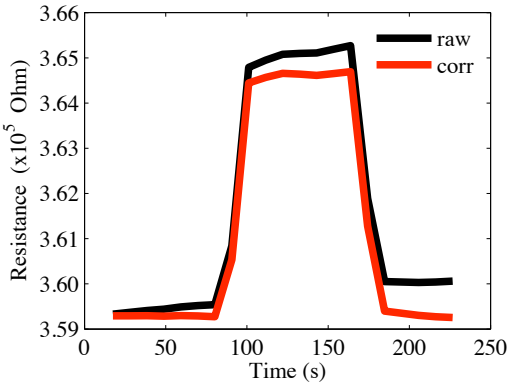


Figure S3. Relative differential resistance response as a function of $P/P°$ for a Au-C8 sensor.

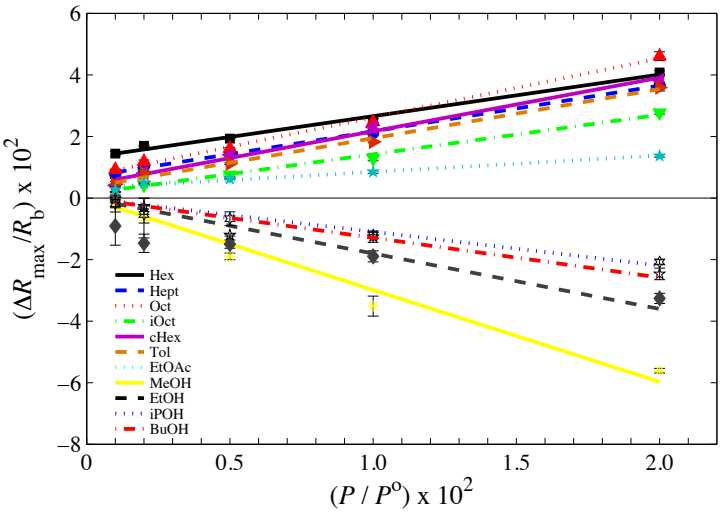


Figure S4. Optical spectra for a Au-C8 film during exposure to air (5 L min^{-1}) and ethanol at $P°$. No change in the plasmon resonance is observed. A red-shift in the plasmon resonance would have indicated an increase of the dielectric constant of the film.

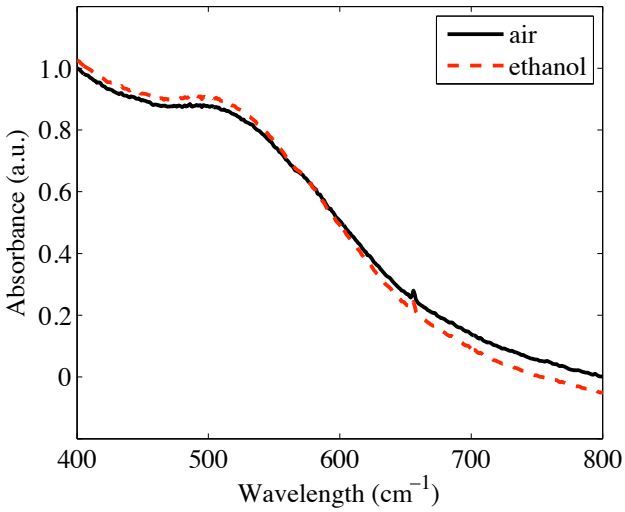
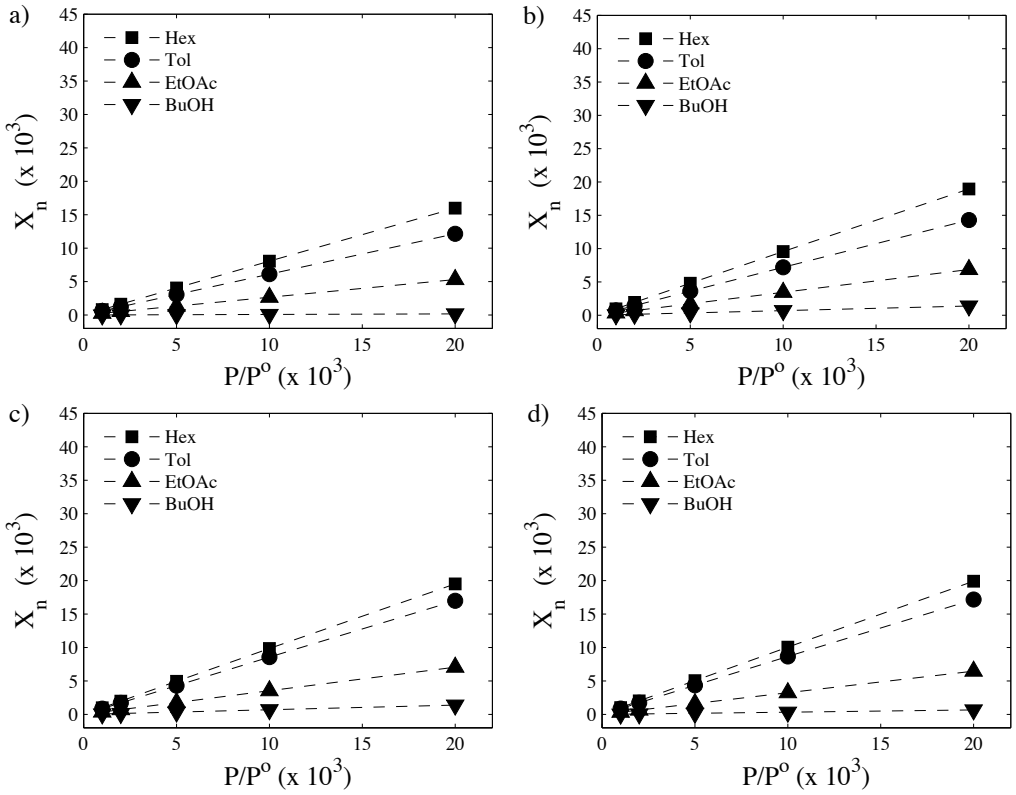


Figure S5. Mole ratio, X_n, between the moles of sorbed analyte sorbed and the moles of ligands in the film, as a function of $P/P°$, for Hex, Tol, EtOAc and BuOH; a) Au-C4, b) Au-C5, c) Au-C6, d) Au-C7, e) Au-C8, f) Au-C9, g) Au-C10, h) Au-C11.



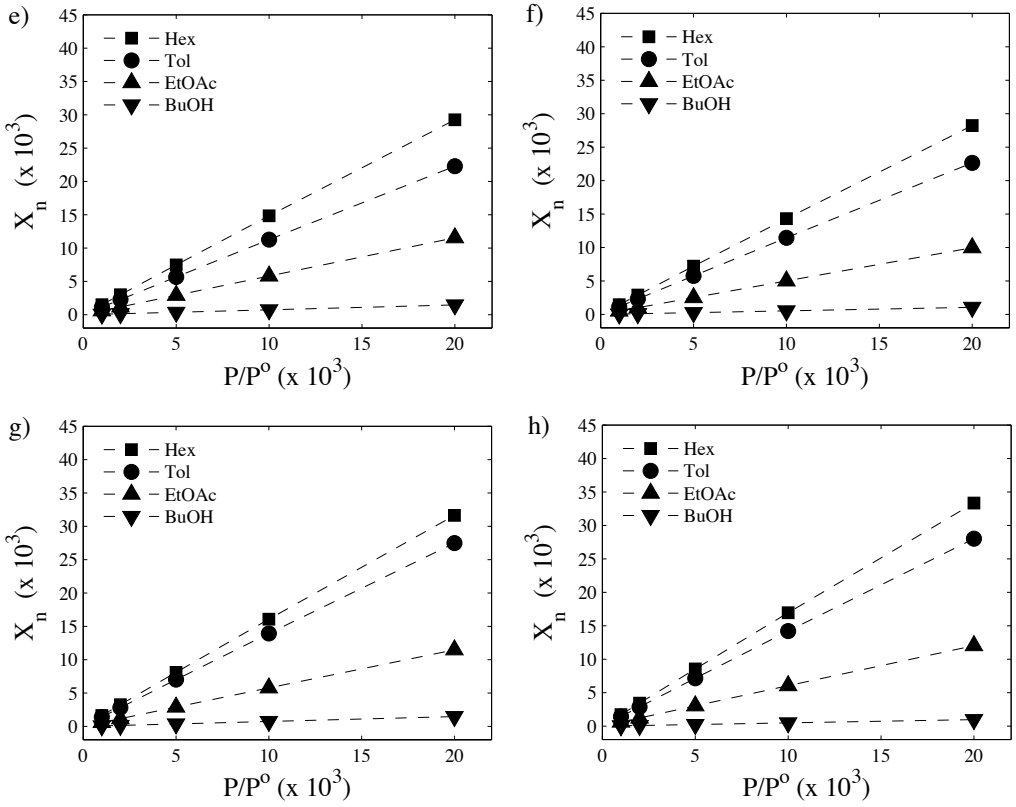
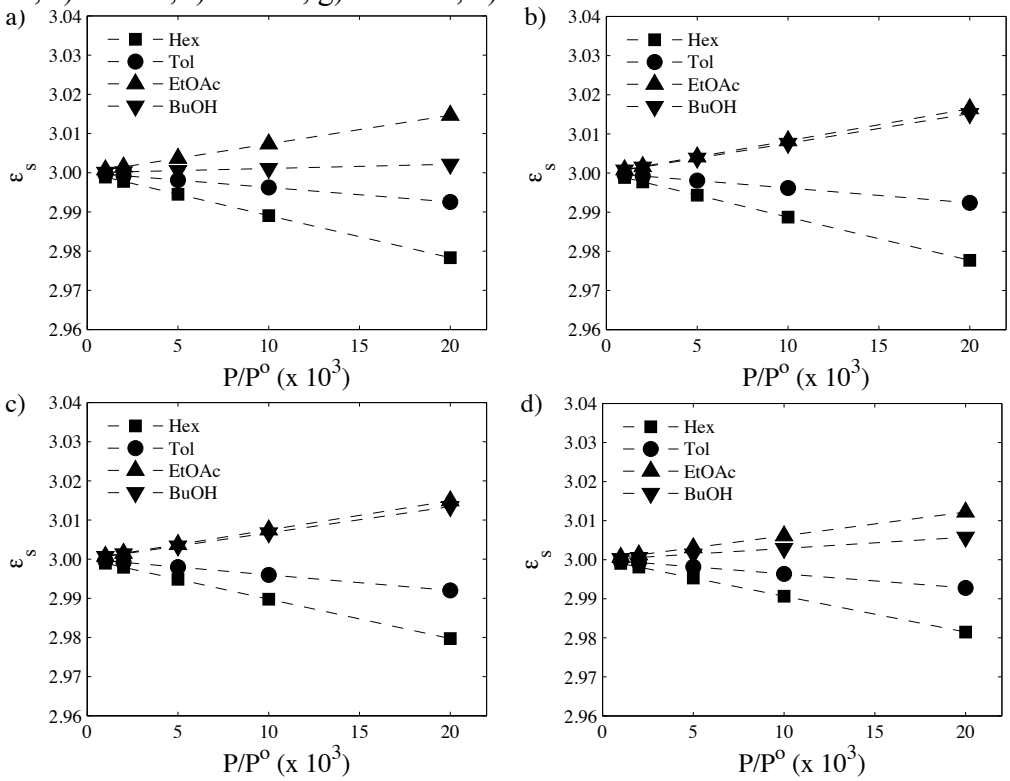

e)
f)
g)
h)
Hex
Tol
EtOAc
BuOH
X_n (x 10^3)
P/P^o (x 10^3)
0
5
10
15
20
25
30
35
40
45

Figure S6. Static dielectric constant, ε_s, of the ligand/analyte organic interface as a function of $P/P°$ for Hex, Tol, EtOAc and BuOH; a) Au-C4, b) Au-C5, c) Au-C6, d) Au-C7, e) Au-C8, f) Au-C9, g) Au-C10, h) Au-C11.



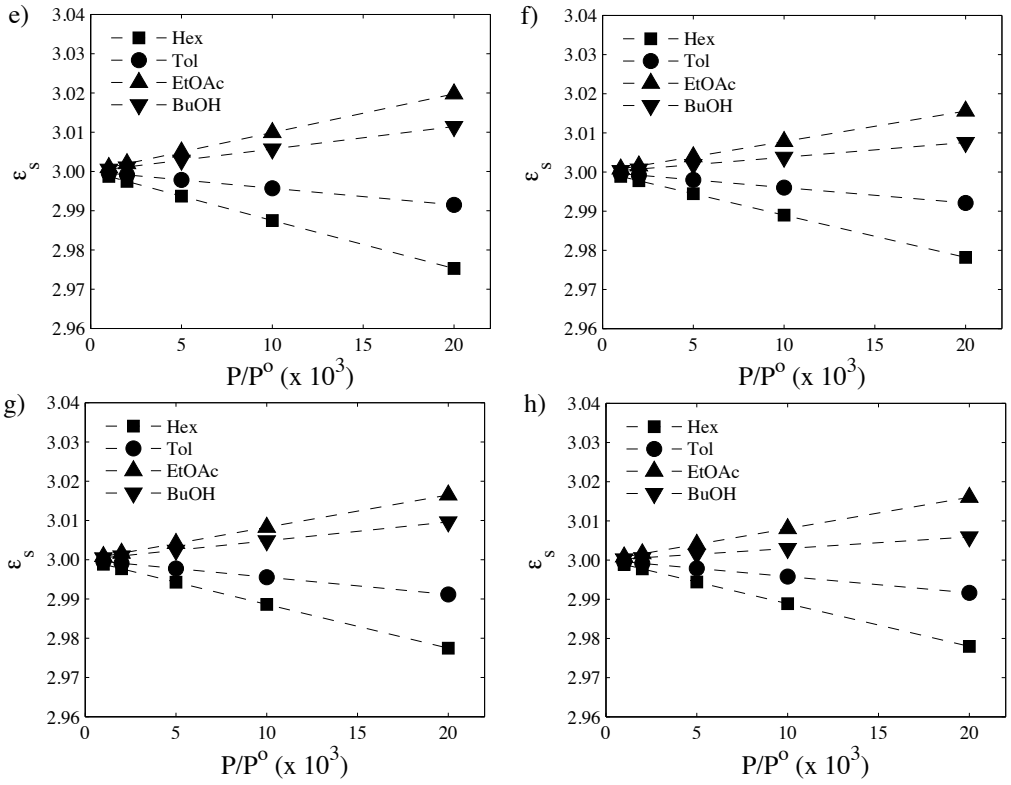

e)
f)
g)
h)
Hex
Tol
EtOAc
BuOH
ε_s
P/P^o (x 10^3)

Figure S7. Scanning electron micrographs of a Au-C8 film that was treated under different vapors. Micrograph a) shows the an as prepared Au-C8 film, micrograph b) shows a film that was presented to a saturated Hex vapor stream for 12 h, micrograph c) shows a film that was presented to a saturated EtOH vapor stream for 12 h.